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**CHEMICAL PROCESS SYSTEMS
LABORATORY**

A Modeling of Semi-Batch Reactors for
Melt Transesterification of Dimethyl
Terephthalate with Ethylene Glycol

by

K.Y. Choi

RESEARCH REPORT

CHEMICAL PROCESS SYSTEMS ENGINEERING LABORATORY

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TRANSESTERIFICATION OF DIMETHYL TEREPHTHALATE
WITH ETHYLENE GLYCOL

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A Modelling of Semi-Batch Reactors for Melt
Transesterification of Dimethyl Terephthalate
with Ethylene Glycol

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ABSTRACT

A mathematical model of a semi-batch reactor has been developed to investigate the oligomerization reactions in the melt transesterification of dimethyl terephthalate with ethylene glycol catalyzed by metal acetate catalyst. The detailed kinetic scheme based on the molecular species model is used to estimate the conversion of methyl ester groups and the concentrations of various oligomeric species. The numerical simulation of the model shows that the oligomerization reactions lower the overall conversion of methyl ester end groups. Effects of ethylene glycol/dimethyl terephthalate mole ratios, reaction temperature and catalyst concentration on the conversion, oligomer concentration, oligomer molecular weight and molecular weight distribution have also been analyzed.

I. INTRODUCTION

Fine tuning the properties of thermoplastic polyesters is becoming more important than ever in recent years. This is due mainly to diversified and varying demands for high performance plastics for extrusion and injection molding. For example, there is a continuing demand from the marketplace for polyesters of high heat resistance, modulus and strength, and impact strength. Here, thermoplastic polyesters imply condensation polymerization products that are characterized by many ester linkages distributed along the polymer backbone. Among the many thermoplastic polyesters, polyethylene terephthalate (PET) is one of the fastest growing for various applications.

PET can be manufactured by three different routes depending upon the starting raw materials: dimethyl terephthalate (DMT) - ethylene glycol (EG) route, terephthalic acid (TPA) - EG route, and TPA -ethylene oxide route. Although TPA - EG route offers some advantages over the more widely used DMT - EG route, DMT is still the preferred raw material for PET and polybutylene terephthalate (PBT) [1]. High molecular weight PET is prepared by three steps: melt transesterification of DMT with EG in the presence of metal acetate catalyst at about 180 - 200^o C and 1 atm, prepolycondensation at 250 -300^o C and 10 - 25 torr, and finishing polymerization at high vacuum (~1.0 torr) in specially designed film reactors. Because of such one-way interacting nature of the polymerization process, the performance of both

melt transesterification and prepolymerization reactors influence the performance of the finishing polymerization reactors and the quality of resulting polymers. Thus, understanding the behavior of each reaction step is very important for the optimal operation of the reactors.

The product of the transesterification reaction consists of monomers (mono (hydroxyethyl) terephthalate (MHET) and bis (hydroxyethyl) terephthalate (BHET)), and very low molecular weight polymers (i.e. oligomers). Ester interchange catalysts commonly used are divalent salts of manganese, zinc, cobalt, magnesium, or calcium.

Modelling of semi-batch and continuous transesterification processes has been reported recently by Ravindranath and Mashelkar [2-5] and Kumar and coworkers [6]. Most of their works utilize the functional group models which yield overall concentrations of different functional end groups. Although various side reactions have been considered in their models, no prediction of oligomer formation has been made. According to the literature on the melt transesterification of DMT with EG, oligomerizations do not occur up to about 80 - 88% conversion when excess ethylene glycol is used (e.g. $[EG]/[DMT] > 2.0$) [7-13]. In many industrial transesterification processes, the reaction is driven to higher conversion with $[EG]/[DMT]$ ratio of about 1.5 - 2.0. Thus, it is likely that some oligomers will be present in the reaction mixture under such operating conditions. Formation of oligomers has also been observed in industrial reactors [14]. However, quantitative analysis of oligomer formation reactions and experimental data of the oligomerization

have not been reported in the open literature. Therefore, it is of interest to investigate the oligomer formation reactions and their effect on the performance of the melt transesterification reactor.

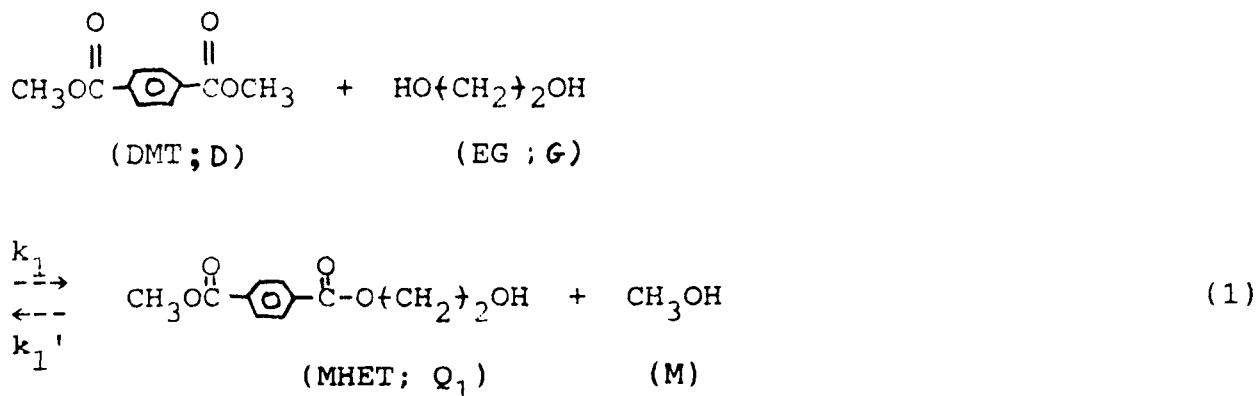
In this paper, we shall develop a kinetic scheme for metal acetate catalyzed transesterification of DMT with EG in a semi-batch reactor. Here, transesterification byproduct (methanol) is continuously removed from the reactor through distillation column. The molecular species model is employed in our modelling in order to predict the composition of oligomer mixtures. The effect of key reactor operating parameters such as $[EG]/[DMT]$ ratio, catalyst concentration and reaction temperature on the reactor performance will be discussed.

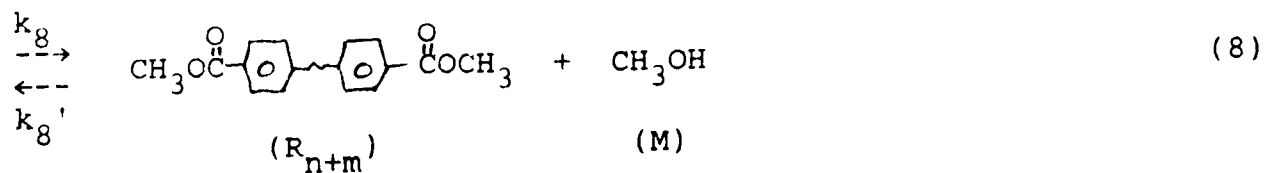
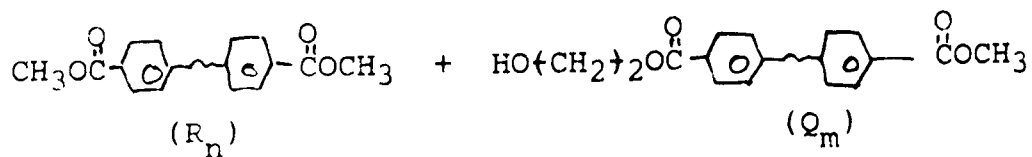
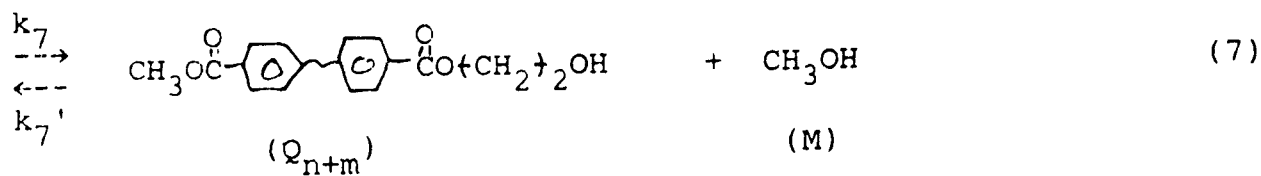
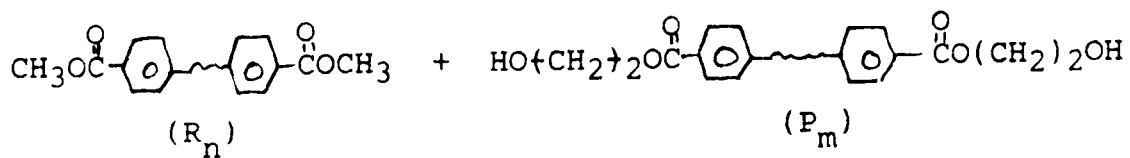
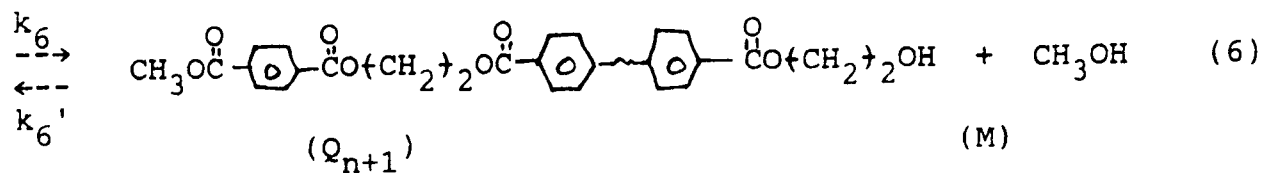
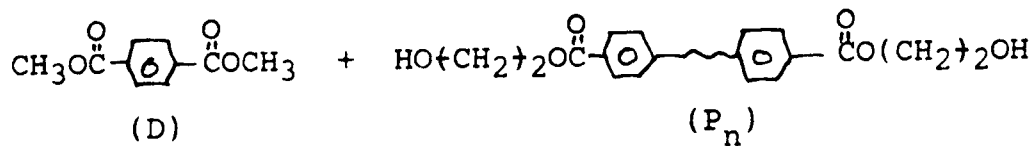
II. MODEL DEVELOPMENT

The main product of the transesterification reaction is bis(hydroxyethyl) terephthalate (BHET) when the oligomerization reactions are absent. BHET is high boiling, very corrosive, hard to pump, and tends to polymerize during distillation. The model we shall develop will consider all possible ester exchange reactions or transesterifications so that not only the concentration of oligomers but also the average degree of oligomerization can be computed. The catalyst system considered in the present work is zinc acetate catalyst which is the most widely used in many industrial processes. Our kinetic model can be extended easily to the transesterification of DMT with 1,4-butanediol for PBT manufacture.

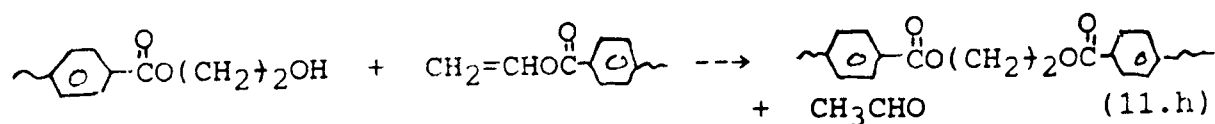
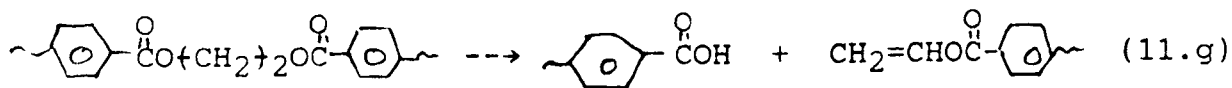
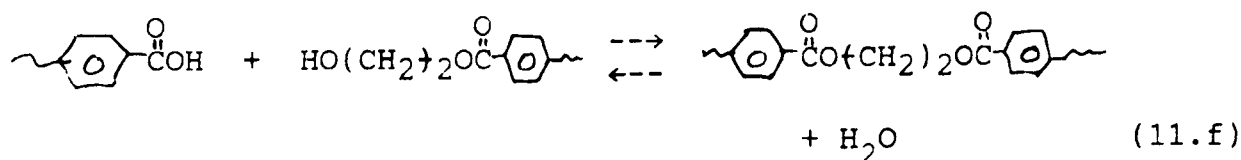
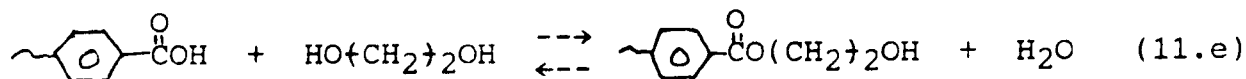
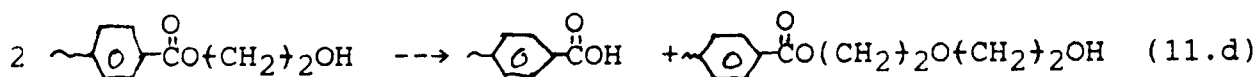
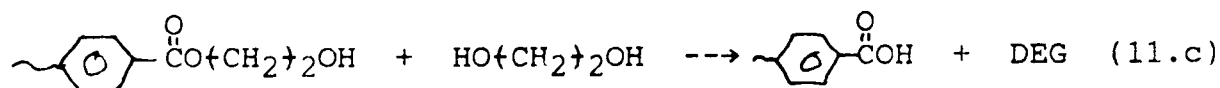
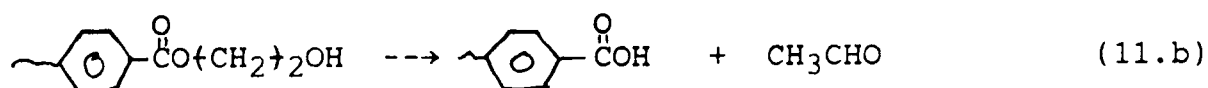
In the first stage melt transesterification reactor, the following reactions occur in the presence of metal acetate catalyst:

(A) Formation of MHET and BHET:





However, the polymerization rate will be very low at normal transesterification conditions (i.e. $\sim 200^\circ$ C and ambient pressure). Thus, the above polycondensation reaction will not be included in our kinetic scheme. Also ignored are some side reactions which generate small amounts of acetaldehyde, diethylene glycol (DEG), water and vinyl groups. These reactions have negligible effects on the oligomerization reactions.



As indicated in Eqs. (1)-(10), those metal acetate catalyzed reactions are essentially reversible; however, the condensation byproduct, viz., methanol, is distilled off continuously from the reactor to promote the forward reactions. At typical transesterification conditions ($180\sim 200^{\circ}\text{C}$ and 1 atm), the efficiency of methanol removal through distillation is quite high and the reaction mixture is not viscous. Thus, methanol concentration in the liquid (or melt) phase will be negligibly small. Consequently, we can ignore the effect of reverse reactions without making significant errors. It should be noted that such assumption may lead to somewhat conservative results, i.e., the highest possible conversion.

Another important factor in modelling semi-batch transesterification reactor is the reduction in reaction volume due to continuous removal of methanol from the reactor. Such volume decrease will result in a relative increase in effective catalyst concentration. For a given transesterification catalyst system, variation in catalyst concentration due to volume change will be reflected in the rate constants given by the Arrhenius form

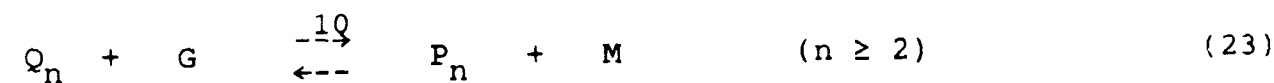
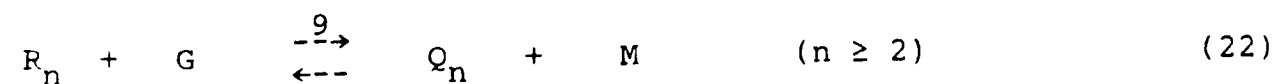
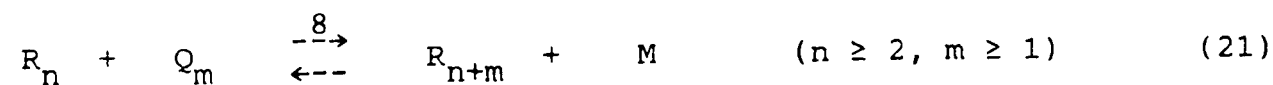
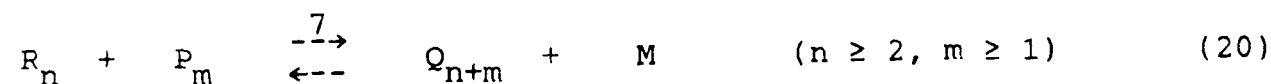
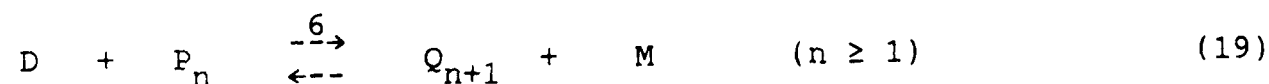
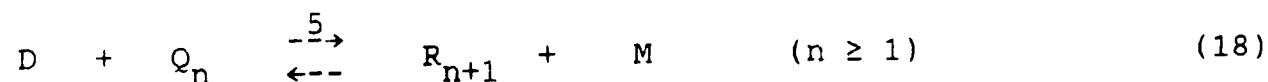
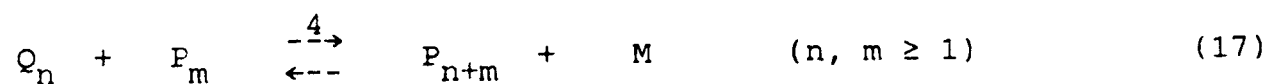
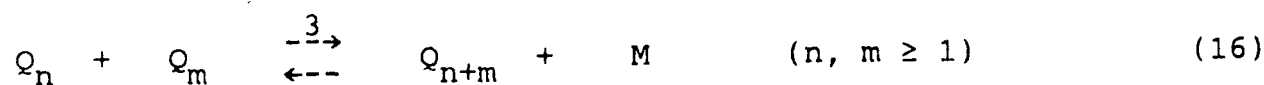
$$k_j = k_{j0} \exp(-E_j/RT) \quad (12)$$

in which the catalyst concentration, $[C^*]$, is implicitly included in the rate constants as follows:

$$k_{j0} = \hat{k}_{j0} [C^*] = \hat{k}_{j0} N^*/V \quad (13)$$

where N^* represents the total number of moles of catalyst in the reactor and V the reactor volume. Thus, effective rate constants for the transesterification will increase as conversion increases. We also assume no catalyst deactivation. The first order dependence of the transesterification rate on the catalyst concentration has been reported in the literature [7].

Now, reactions (1)-(10) can be rewritten in compact form as follows:



In the reaction schemes above, Q_n represents the oligomer chains of n -repeating units carrying both methyl ester end group and hydroxyl end group, and P_n the oligomer chains carrying hydroxyl end groups on both chain ends. End-capped oligomers, R_n , have methyl ester groups on both chain ends. In order to obtain high molecular weight polymers in the polycondensation stage, it is desirable to maximize the conversion of methyl ester end groups during the transesterification stage.

In the following development, we shall use the molecular species model in which each chemical species is considered as an independent reactive compound. One of the principal advantages of using the molecular species model is that complete composition distribution of the transesterification products can be determined by using the molecular weight moment equations and kinetic equations. Although the functional group model which only takes into account the reactions between the functional end groups is relatively simple and straightforward to use for the prediction of overall conversions, such model does not yield an information on the oligomerizations and the detailed product composition profiles.

Under isothermal reaction conditions, the component material balances take the following form:

$$\frac{d(VD)}{dt} = V (-k_1 DG - k_5 DQ - k_6 DP) \quad (24)$$

$$\frac{d(VG)}{dt} = V (-k_1 DG - k_2 GQ_1 - k_9 GR - k_{10} GQ) \quad (25)$$

$$\frac{d(VQ_1)}{dt} = V (k_1 DG - k_2 GQ_1 - k_3 Q_1 Q - k_4 Q_1 P - k_5 DQ_1 - k_8 Q_1 R) \quad (26)$$

$$\frac{d(VP_1)}{dt} = V (k_2 GQ_1 - k_4 P_1 Q - k_6 P_1 D - k_7 P_1 R) \quad (27)$$

$$n \geq 2;$$

$$\frac{d(VP_n)}{dt} = V (-k_4 P_n Q + k_4 \sum_{j=1}^{n-1} P_j Q_{n-j} - k_6 DP_n - k_7 P_n R + k_{10} GQ_n) \quad (28)$$

$$\begin{aligned} \frac{d(VQ_n)}{dt} = V & (-k_3 Q_n Q + \frac{k_3}{2} \sum_{j=1}^{n-1} Q_j Q_{n-j} - k_4 Q_n P - k_5 Q_n D + k_6 DP_{n-1} \\ & + k_7 \sum_{j=1}^{n-1} P_j R_{n-j} - k_8 Q_n R + k_9 GR_n - k_{10} GQ_n) \end{aligned} \quad (29)$$

$$\frac{d(VR_n)}{dt} = V (k_5 DQ_{n-1} - k_7 PR_n + k_8 \sum_{j=2}^{n-1} R_j Q_{n-j} - k_9 GR_n - k_8 QR_n) \quad (30)$$

$$\frac{dV}{dt} = \frac{-V}{\rho_M} \left\{ \begin{aligned} & k_1 DG + k_3 Q^2 + k_4 PQ + k_5 DQ + k_6 DP + k_7 PR + k_8 QR \\ & + k_9 GR + k_{10} GQ \end{aligned} \right\} \quad (31)$$

where upper case symbols represent bulk molar concentrations of species in the reaction mixture and V the volume of reaction mixture. Since the reaction volume decreases with conversion due to continuous removal of methanol, it will be more convenient to use the material balance equations based on the number of moles of each species in the reactor. Thus, the following transformation of variables is made:

$$\begin{aligned} D_1 &\equiv VD, & g &\equiv VG, & p_1 &\equiv VP_1, & q_1 &\equiv VQ_1 \\ p_n &\equiv VP_n, & q_n &\equiv VQ_n, & r_n &\equiv VR_n \end{aligned}$$

With these new variables, the material balance equations are reduced to the following form:

$$\frac{dD}{dt} = \frac{1}{V} (-k_1 Dg - k_5 Dq - k_6 Dp) \quad (32)$$

$$\frac{dg}{dt} = \frac{1}{V} (-k_1 Dg - k_2 q_1 g - k_9 gr - k_{10} gq) \quad (33)$$

$$\frac{dq_1}{dt} = \frac{1}{V} \left\{ k_1 Dg - k_2 gq_1 - k_3 q_1 q - k_4 p q_1 - k_5 Dq_1 - k_8 q_1 r \right\} \quad (34)$$

$$\frac{dp_1}{dt} = \frac{1}{V} \left\{ k_2 gq_1 - k_4 p_1 q - k_6 p_1 D - k_7 p_1 r \right\} \quad (35)$$

$n \geq 2$:

$$\frac{dp_n}{dt} = \frac{1}{V} \left\{ -k_4 p_n q + k_4 \sum_{j=1}^{n-1} p_j q_{n-j} - k_6 D p_n - k_7 p_n r + k_{10} g q_n \right\} \quad (36)$$

$$\begin{aligned} \frac{dq_n}{dt} = \frac{1}{V} \left\{ -k_3 q_n q + \frac{k_3}{2} \sum_{j=1}^{n-1} q_j q_{n-j} - k_4 q_n p - k_5 D q_n + k_6 D p_{n-1} \right. \\ \left. + k_7 \sum_{j=1}^{n-1} p_j r_{n-j} - k_8 q_n r + k_9 g r_n - k_{10} g q_n \right\} \quad (37) \end{aligned}$$

$$\frac{dr_n}{dt} = \frac{1}{V} \left\{ k_5 D q_{n-1} - k_7 r_n p - k_8 q r_n + k_8 \sum_{j=1}^{n-1} r_j q_{n-j} - k_9 g r_n \right\} \quad (38)$$

$$\begin{aligned} \frac{dV}{dt} = \frac{-1}{V \rho_M} \left\{ k_1 Dg + k_3 q^2 + k_4 pq + k_5 Dq + k_6 Dp + k_7 pr + k_8 qr \right. \\ \left. + k_9 gr + k_{10} gq \right\} \quad (39) \end{aligned}$$

The degree of oligomerization is computed by using the molecular weight moments which are defined as follows:

$$\lambda_{P,k} \equiv \sum_{n=1}^{\infty} n^k p_n \quad (40.a)$$

$$\lambda_{Q,k} \equiv \sum_{n=1}^{\infty} n^k q_n \quad (40.b)$$

$$\lambda_{R,k} \equiv \sum_{n=2}^{\infty} n^k r_n \quad (40.c)$$

Using the material balances (Eqs. (32)-(39)) and the moments defined above, one can derive the following molecular weight moment equations for various oligomeric species:

$$\frac{d\lambda_{p,0}}{dt} = \frac{1}{V} \left\{ k_2 g q_1 - k_6 D p - k_7 p r + k_{10} g (q - q_1) \right\} \quad (41)$$

$$\begin{aligned} \frac{d\lambda_{p,1}}{dt} = \frac{1}{V} \left\{ k_2 g q_1 + k_4 p \lambda_{Q,1} - k_6 D \lambda_{p,1} - k_7 r \lambda_{p,1} \right. \\ \left. + k_{10} g (\lambda_{Q,1} - q_1) \right\} \end{aligned} \quad (42)$$

$$\begin{aligned} \frac{d\lambda_{p,2}}{dt} = \frac{1}{V} \left\{ k_2 g q_1 + k_4 (p \lambda_{Q,2} + 2 \lambda_{p,1} \lambda_{q,1}) - k_6 D \lambda_{p,2} \right. \\ \left. - k_7 r \lambda_{p,2} + k_{10} g (\lambda_{Q,2} - q_1) \right\} \end{aligned} \quad (43)$$

$$\begin{aligned} \frac{d\lambda_{Q,0}}{dt} = \frac{1}{V} \left\{ k_1 D g - k_2 g q_1 - \frac{k_3}{2} q^2 - k_4 p q - k_5 D q + k_6 D p \right. \\ \left. + k_7 p r - k_8 q r + k_9 q r - k_{10} g (q - q_1) \right\} \end{aligned} \quad (44)$$

$$\begin{aligned}
\frac{d\lambda_{Q,1}}{dt} &= \frac{1}{V} \left\{ k_1 Dg - k_2 gq_1 - k_4 P\lambda_{Q,1} - k_5 D\lambda_{Q,1} \right. \\
&\quad + k_6 D(\lambda_{P,1} + p) + k_7 (P\lambda_{R,1} + r\lambda_{P,1}) \\
&\quad \left. - k_8 r\lambda_{Q,1} + k_9 g\lambda_{R,1} - k_{10} g(\lambda_{Q,1} - q_1) \right\} \quad (45)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{Q,2}}{dt} &= \frac{1}{V} \left\{ k_1 Dg - k_2 gq_1 + k_3 \lambda_{Q,1}^2 - k_4 P\lambda_{Q,2} \right. \\
&\quad - k_5 D\lambda_{Q,2} + k_6 D(\lambda_{P,2} + 2\lambda_{P,1} + p) \\
&\quad + k_7 (\lambda_{P,2} p + 2\lambda_{R,1} \lambda_{P,1} + r\lambda_{P,2}) \\
&\quad \left. - k_8 \lambda_{Q,2} r + k_9 g\lambda_{R,2} - k_{10} g(\lambda_{Q,2} - q_1) \right\} \quad (46)
\end{aligned}$$

$$\frac{d\lambda_{R,0}}{dt} = \frac{1}{V} \left\{ k_5 Dq - k_7 pr - k_9 gr \right\} \quad (47)$$

$$\begin{aligned}
\frac{d\lambda_{R,1}}{dt} &= \frac{1}{V} \left\{ k_5 D(\lambda_{Q,1} + q) - k_7 P\lambda_{R,1} \right. \\
&\quad \left. + k_8 (\lambda_{Q,1} r + q\lambda_{R,1}) - k_8 q\lambda_{R,1} - k_9 g\lambda_{R,1} \right\} \quad (48)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{R,2}}{dt} &= \frac{1}{V} \left\{ k_5 D(\lambda_{Q,2} + 2\lambda_{Q,1} + q) - k_7 P\lambda_{P,2} \right. \\
&\quad \left. + k_8 (r\lambda_{Q,2} + 2\lambda_{Q,1} \lambda_{R,1}) - k_9 g\lambda_{R,2} \right\} \quad (49)
\end{aligned}$$

where

$$\left. \begin{aligned} p &= \sum_{n=1}^{\infty} p_n \\ q &= \sum_{n=1}^{\infty} q_n \\ r &= \sum_{n=1}^{\infty} r_n \end{aligned} \right\} \quad (50)$$

The initial conditions for these moment equations are

$$\lambda_{p,k}(0) = \lambda_{q,k}(0) = \lambda_{r,k}(0) = 0, \quad (k = 1, 2, 3) \quad (51)$$

Number and weight average degree of oligomerization are defined by

$$\bar{X}_N = \frac{\lambda_{p,1} + \lambda_{q,1} + \lambda_{r,1}}{\lambda_{p,0} + \lambda_{q,0} + \lambda_{r,0}} \quad (52.a)$$

$$\bar{X}_W = \frac{\lambda_{p,2} + \lambda_{q,2} + \lambda_{r,2}}{\lambda_{p,1} + \lambda_{q,1} + \lambda_{r,1}} \quad (52.b)$$

The average chain lengths of oligomers P_n , Q_n , and R_n are defined by

$$\bar{X}_{N,i} = \lambda_{i,1} / \lambda_{i,0} \quad (i = P, Q, R) \quad (52.c)$$

One of the issues in analyzing the kinetics of transesterification of DMT with EG has been whether the reactive functional end groups on various reactants, intermediates or oligomers have equal reactivities. Although early report by Peebles and Wagner [13] indicates that the transesterification rate constant (k_2) of the zinc acetate catalyzed transesterification of DMT with EG to produce BHET is about three times greater than the rate constant of the first step (ester exchange reaction), many other investigators [7-12] conclude that methyl ester end groups on DMT and MHET are equally reactive. In this work, the reactivities of methyl ester end groups on DMT, MHET and oligomers (Q_n and R_n type) are assumed equal. The reactivities of the hydroxyl end groups on half-esterified DMT (MHET), BHET and oligomers (Q_n and P_n) are assumed to be one half of the reactivity of hydroxyl groups on ethylene glycol [2-6, 10, 11]; i.e.,

$$k_1 = k_2 = k_9 = k_{10} \quad (53)$$

$$k_j = 0.5 k_1 \quad (j = 3, 4, \dots, 8) \quad (54)$$

The following rate constant is used for numerical simulation of the model [2]:

$$k_1 = 4.0 \times 10^7 \exp(-15,000/RT) \quad N^*/V, \text{ l/mol.min.}$$

where N^* denotes initial number of moles of catalyst in the reactor. The modelling equations (Eqs. (32)-(35), (41)-(49)) have been solved simultaneously using the 4th order Runge-Kutta method.

III. RESULTS AND DISCUSSION

Effects of [EG]/[DMT] Ratio

In many industrial PET processes, the selection of the optimum [EG]/[DMT] mole ratio has been known as one of the most important factors in the operation of the transesterification reactors to produce high quality monomers. Figure 1 shows the fractional conversion of total methyl ester groups with reaction time at constant temperature. Here, $[C^*]$ denotes the initial catalyst concentration, as it changes with changing reaction volume. As reported for similar systems (e.g. polybutylene terephthalate process [15]), the higher the [EG]/[DMT] ratio, the faster the reaction rate becomes. Experimentally, the conversion of methyl ester end groups can be determined by monitoring the methanol evolution rate from the reactor.

Figure 2 shows the variation in mole numbers of DMT, MHET (half-esterified DMT) and BHET (fully esterified DMT). It is interesting to note that the amount of DMT in the reactor is a unique function of methyl ester group conversion; however, the formation of both intermediate (MHET) and the final product (BHET) species are rather strongly influenced by the [EG]/[DMT] mole ratios. Moreover, the number average chain length of oligomers (X_n) as shown in Figure 3(a) indicates that using low [EG]/[DMT] ratio results in oligomers of longer chain length as conversion of methyl ester group increases. Also note that mostly dimers are produced when the [EG]/[DMT] ratio is about 2.0-2.5 whereas trimers or oligomers of longer chains are

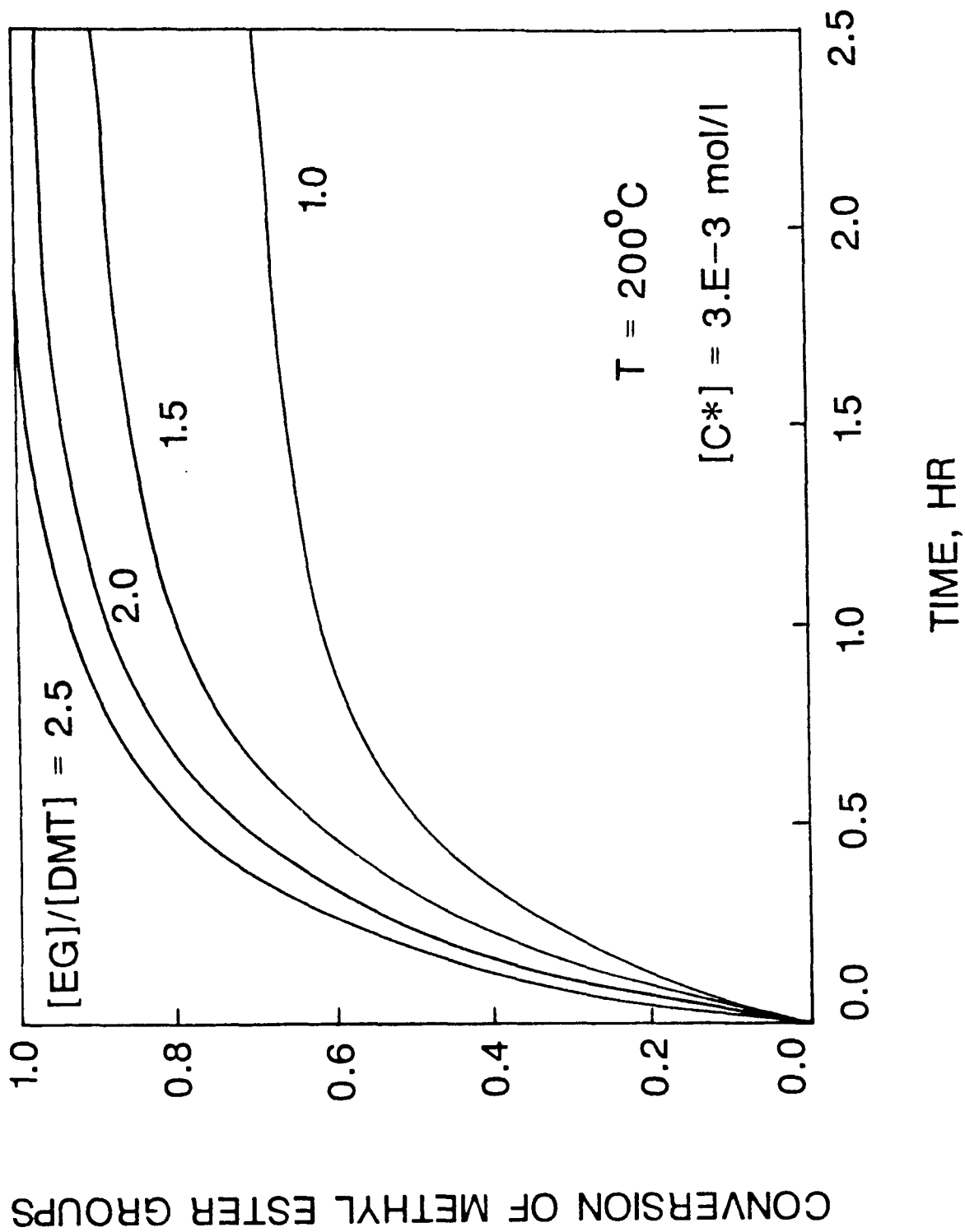


Figure 1 Effect of [EG]/[DMT] mole ratio on the conversion of methyl ester group in a semi-batch reactor.

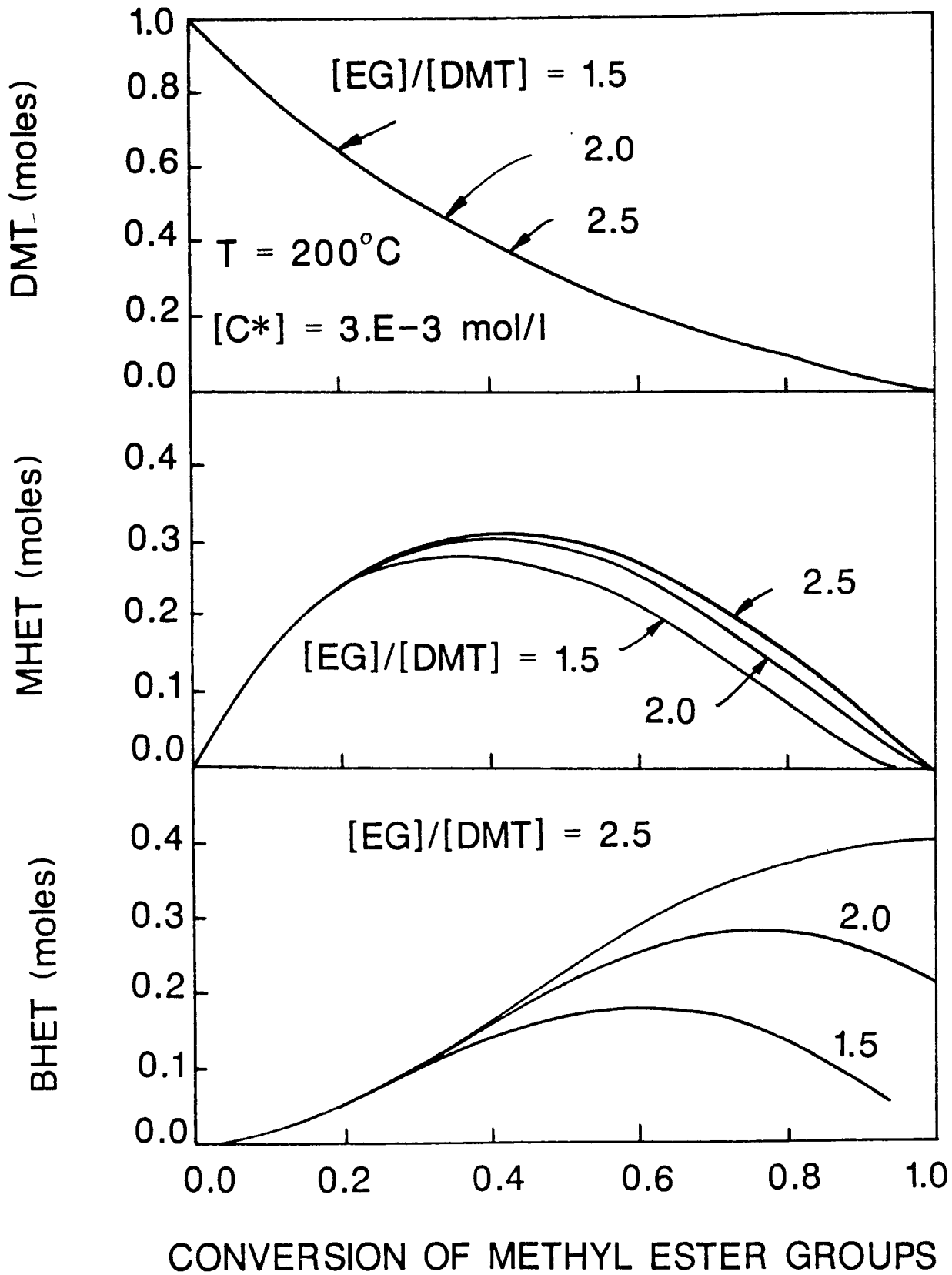


Figure 2 Effect of $[EG]/[DMT]$ ratio on the product distribution.

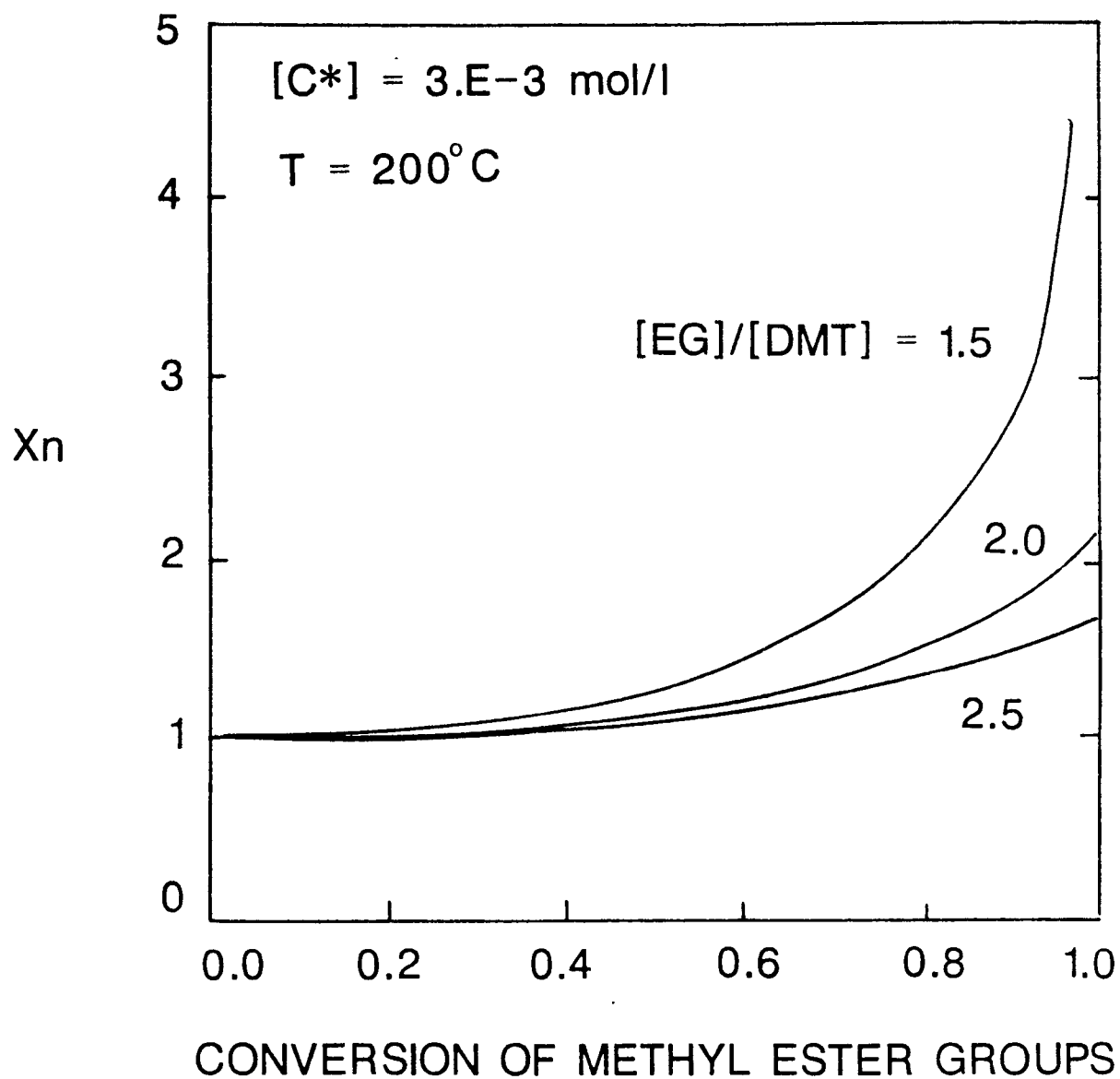


Figure 3 (a) Number average degree of oligomerization for varying [EG]/[DMT] ratios.

produced at lower [EG]/[DMT] ratios. When the conversion is below 80%, X_n is about 1.5 for [EG]/[DMT] ratio of 2.0. This result is in agreement with reported values [16, 17]. In many industrial processes, [EG]/[DMT] mole ratios of about 1.5-2.0 are employed. Our simulation results indicate that for such operating conditions, oligomers having more than two repeating units will be present in the transesterification product when the conversion is above 85%. Figure 3(b) shows the weight average degree of oligomerization for three values of [EG]/[DMT] ratio. Slight broadening of oligomer molecular weight distribution (X_w/X_n) is observed from Figure 3(a) and 3(b) when [EG]/[DMT] mole ratio is less than 2.0.

Figures 4 and 5 represent variation in the average chain lengths of different oligomeric species (P_n , Q_n , R_n) and their total mole numbers for [EG]/[DMT] ratios of 1.5 and 2.5, respectively. Note that average chain length of R_n (end-capped oligomers) is slightly longer than both P_n and Q_n ; however, the amount of R_n -oligomers is negligibly small. It is also observed that near the conversion level of 80% (~ 1 hour), both P_n and Q_n -type oligomers are the main constituents of the oligomer mixture for [EG]/[DMT] = 1.5. Figures 2 and 5 illustrate that when high [EG]/[DMT] ratio is used, dominant product species after 2.5 hours of reaction are P_n and BHET which carry completely esterified end groups. However, increasing the [EG]/[DMT] ratio to unnecessarily high values may not be advantageous from economical point of view. Moreover, the existence of a large quantity of unreacted ethylene glycol from the transesterification step may cause undesirable foaming in the

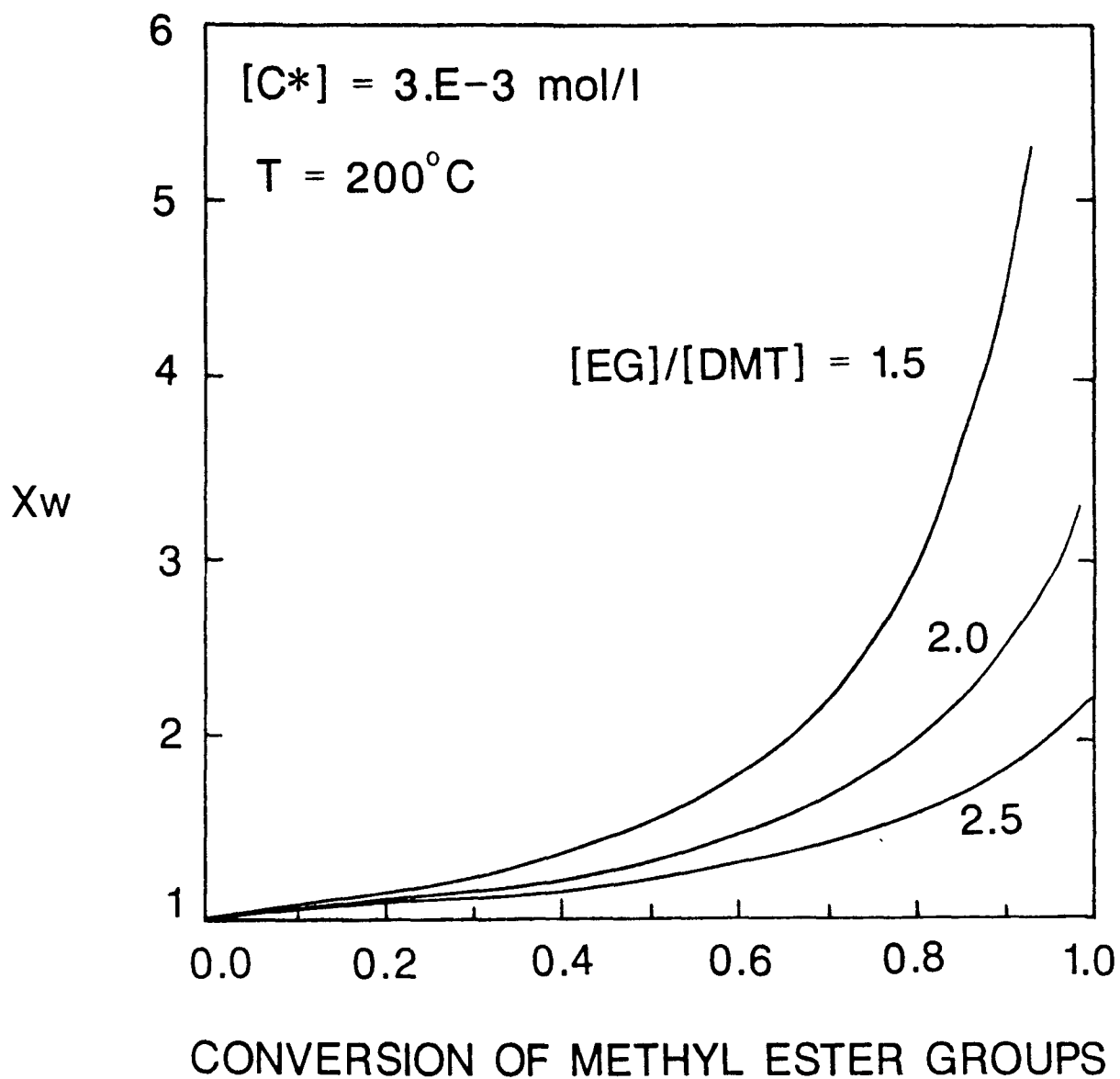


Figure 3 (b) Weight average degree of oligomerization for varying $[\text{EG}]/[\text{DMT}]$ ratios.

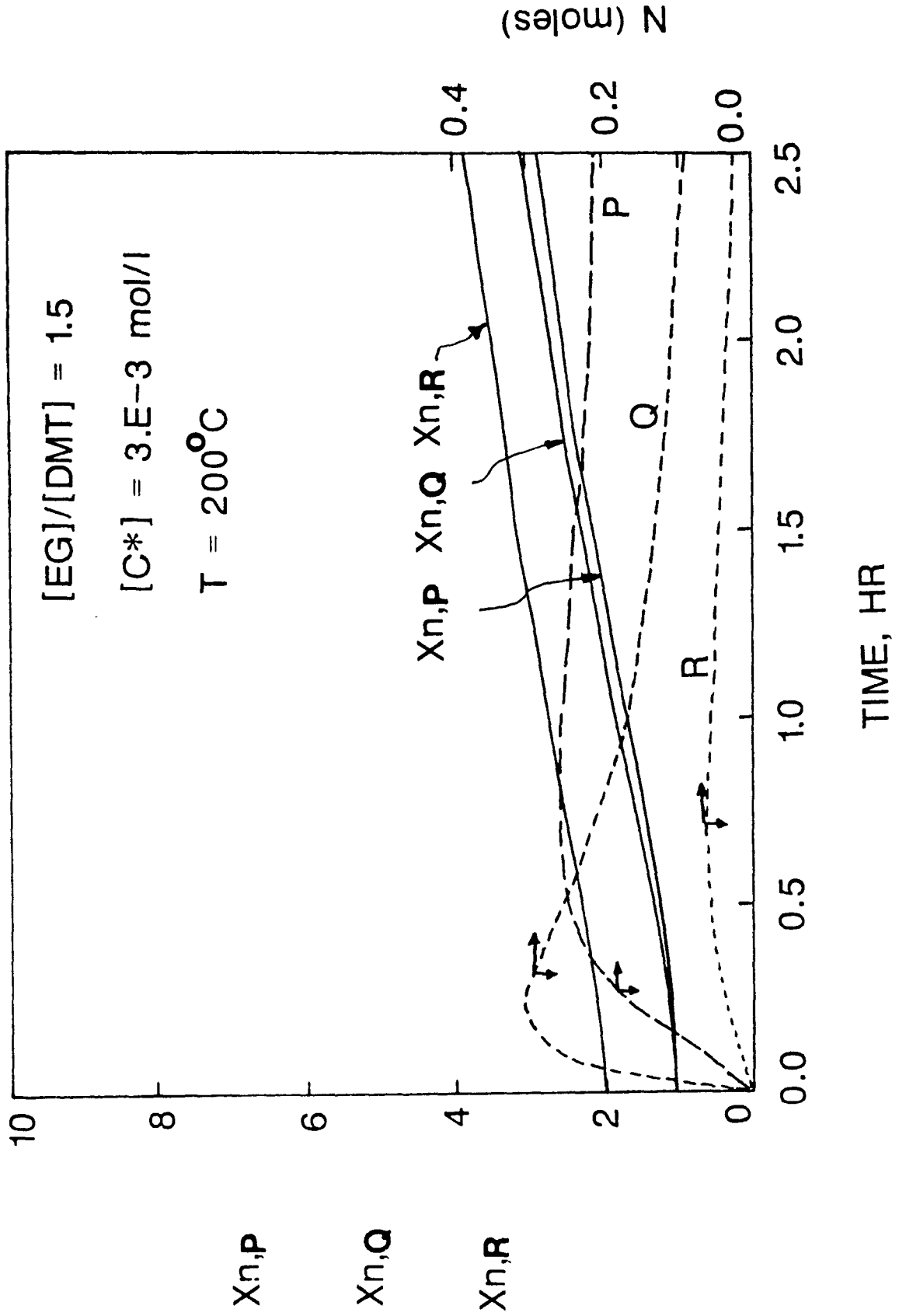


Figure 4 Average chain lengths of oligomers and oligomer concentration distribution for $[EG]/[DMT]=1.5$.

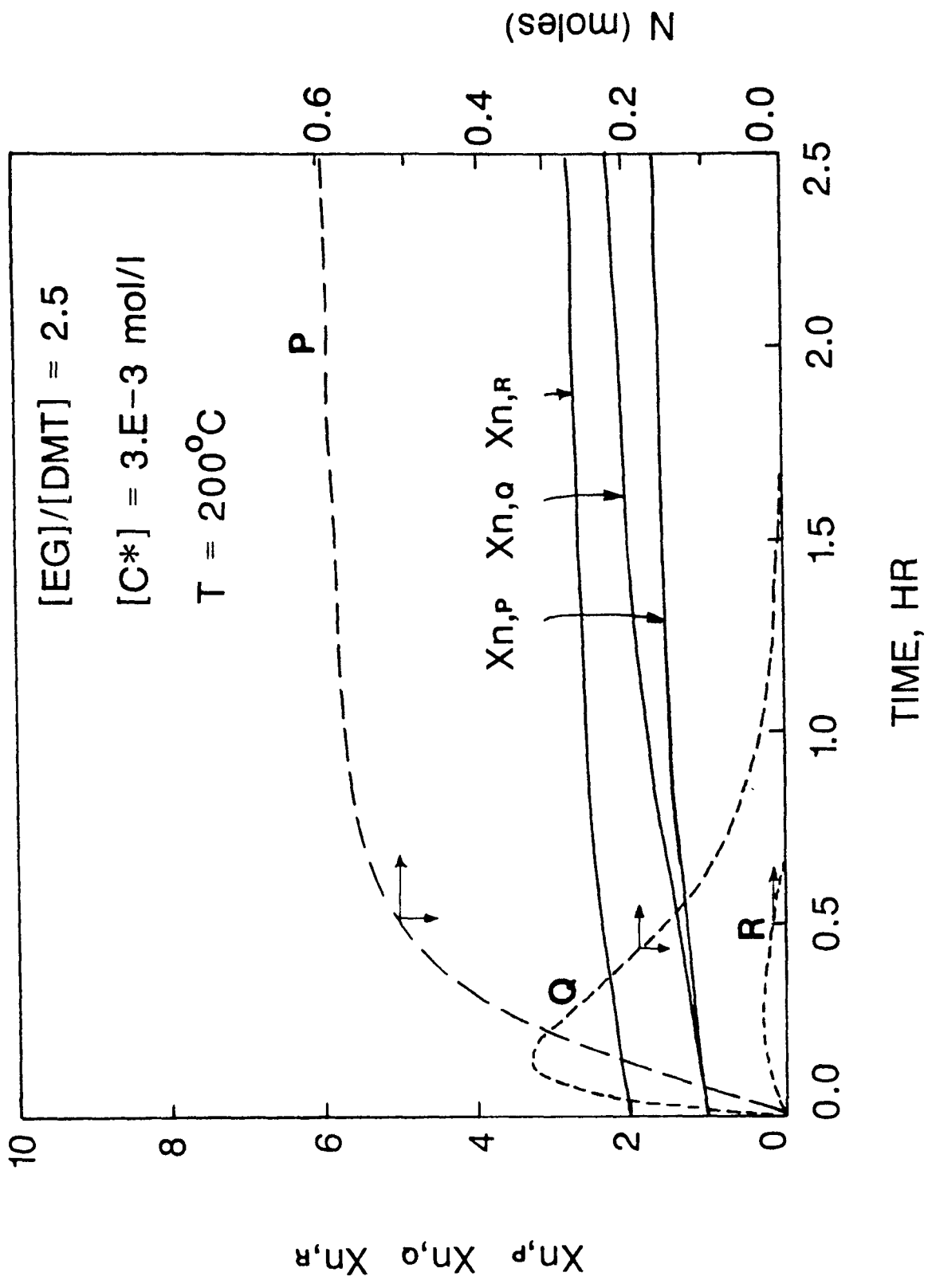


Figure 5 Average chain lengths of oligomers and oligomer concentration distribution for $[EG]/[DMT]=2.5$.

process pipeline between the transesterification reactor and polymerization reactor when the reactors are operated in a continuous manner.

Figure 6 shows the conversion of methyl ester end group with and without the oligomerization reactions (3)-(10). Note that after 2.5 hours the predicted conversion is about 10% less when oligomerization reactions are included. In the absence of oligomerization, higher concentration of fully esterified DMT (i.e., BHET) is produced as indicated in Figure 7 (c.f. Figure 2).

Effect of Catalyst Concentration

The metal acetate catalyst concentration is another important operating parameter. As indicated in Figure 8, overall conversion of methyl ester end groups increases significantly with an increase in catalyst concentration. It has also been found that when the $[EG]/[DMT]$ mole ratio is kept constant, the effects of catalyst concentration on the average oligomer chain lengths (X_n and X_w) are represented by unique curves as shown in Figure 9. Note that even at near 100% conversion of methyl ester groups, the average oligomer chain length is only about 2. Figure 10 shows the variation in total mole numbers of DMT, MHET and BHET with conversion for various catalyst concentrations ($[C^*] = 0.5 \sim 3.0 \times 10^{-3}$ mol/l). Again, the composition profiles are collapsed into unique trajectories which are independent of catalyst concentration. The similar curves are also obtained for total mole numbers of oligomeric species, P_n , Q_n and R_n as

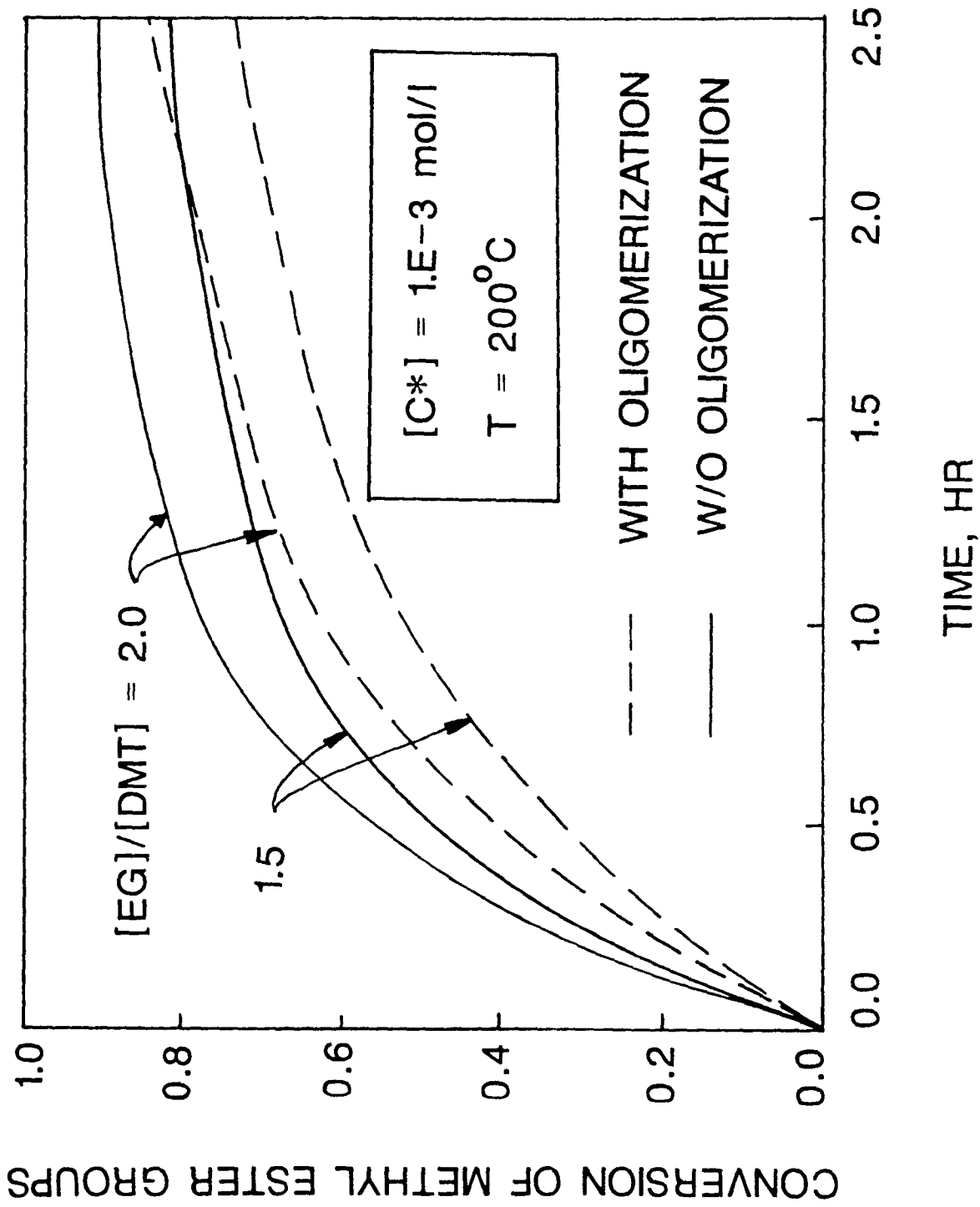


Figure 6 Conversion of methyl ester groups with and without oligomerization reactions.

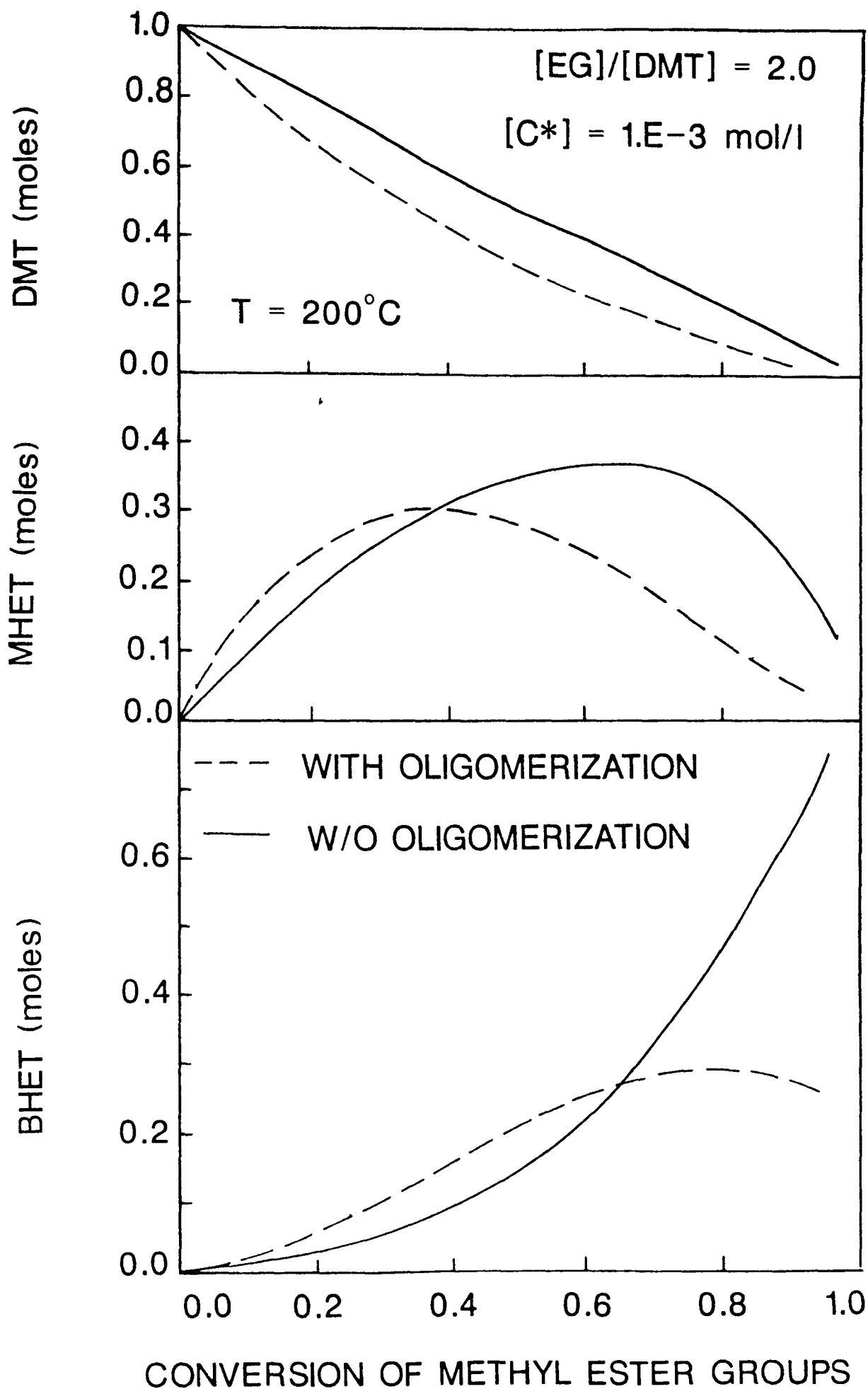


Figure 7

Formation of MHET and BHET in the absence of oligomerization reactions; $[C^*] = 1.E-3 \text{ mol/l}$, 200°C .

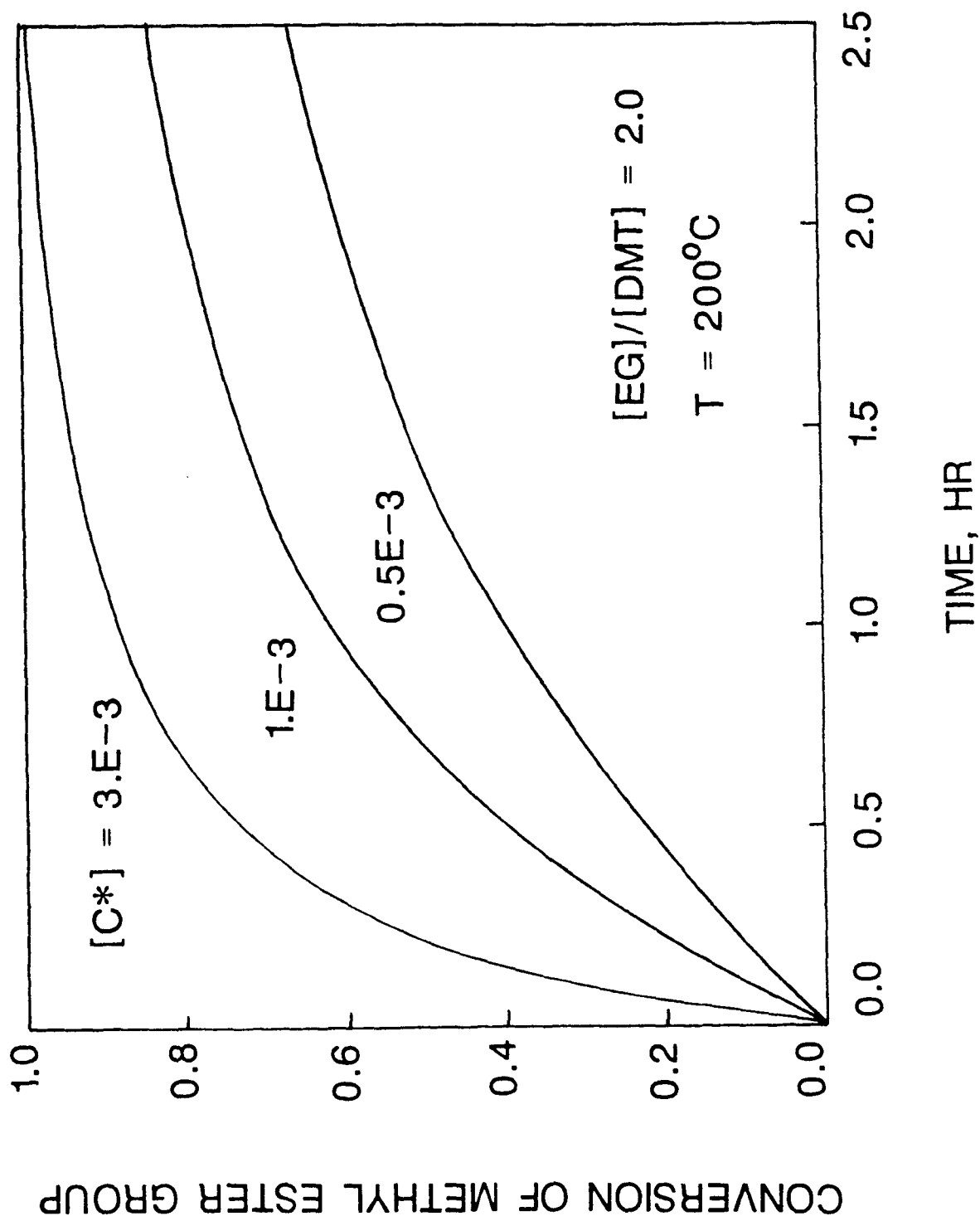


Figure 8 Effect of catalyst concentration on the conversion of methyl ester end groups.

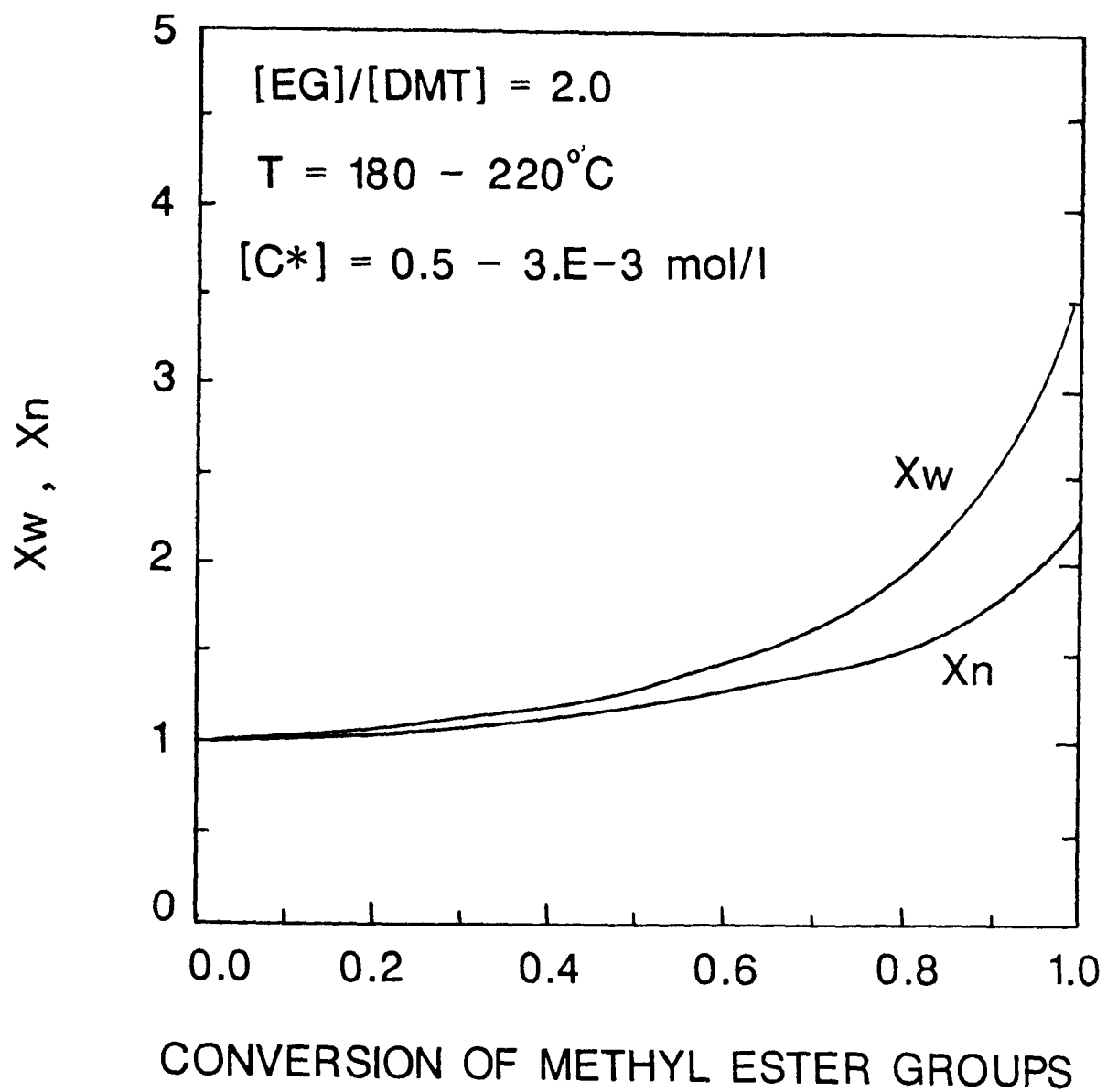


Figure 9 Average oligomer chain lengths for varying catalyst concentrations and temperature, $[EG]/[DMT]=2.0$.

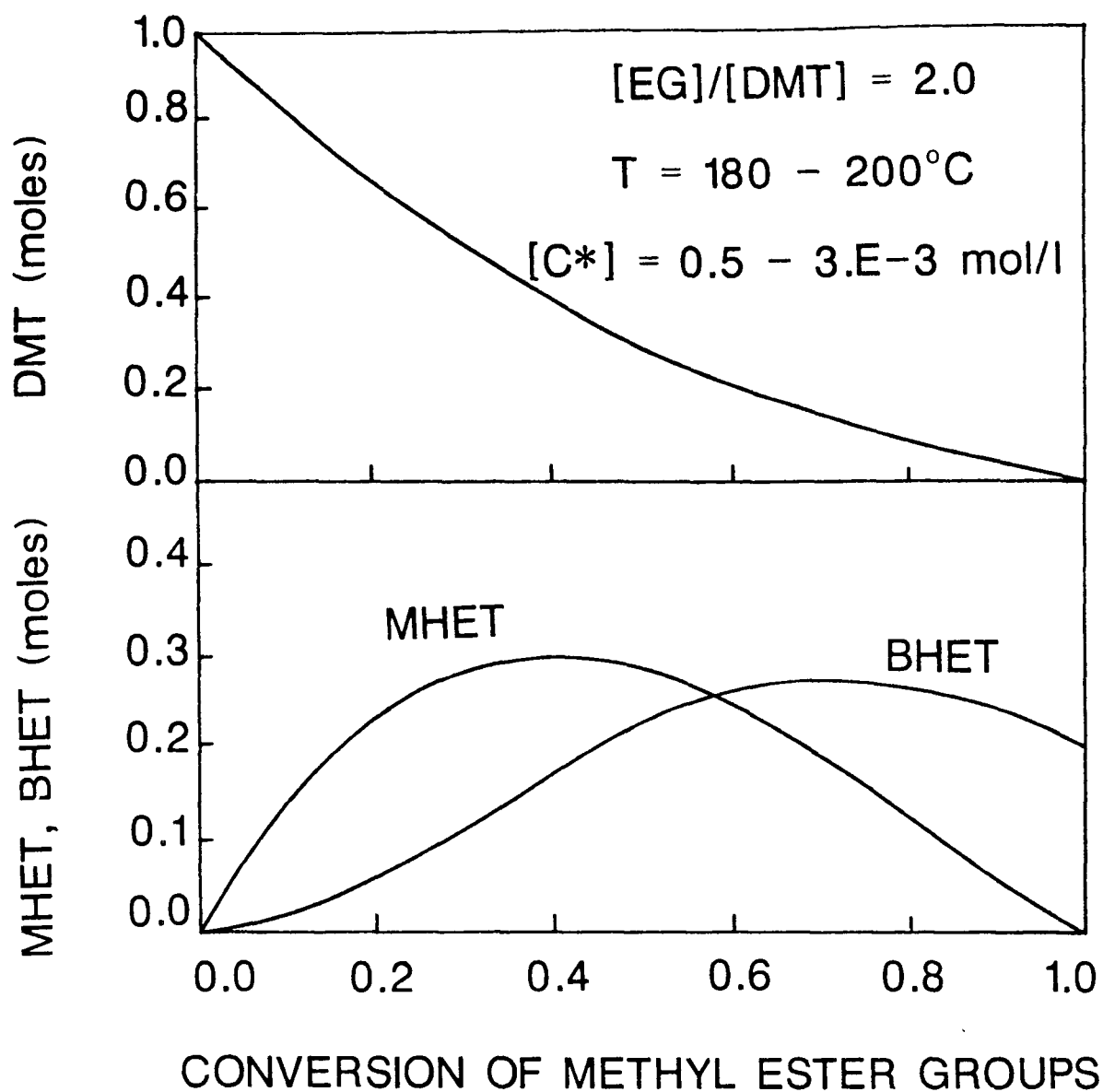


Figure 10 Product composition distribution for varying catalyst concentration and temperatures, $[EG]/[DMT]=2.0$.

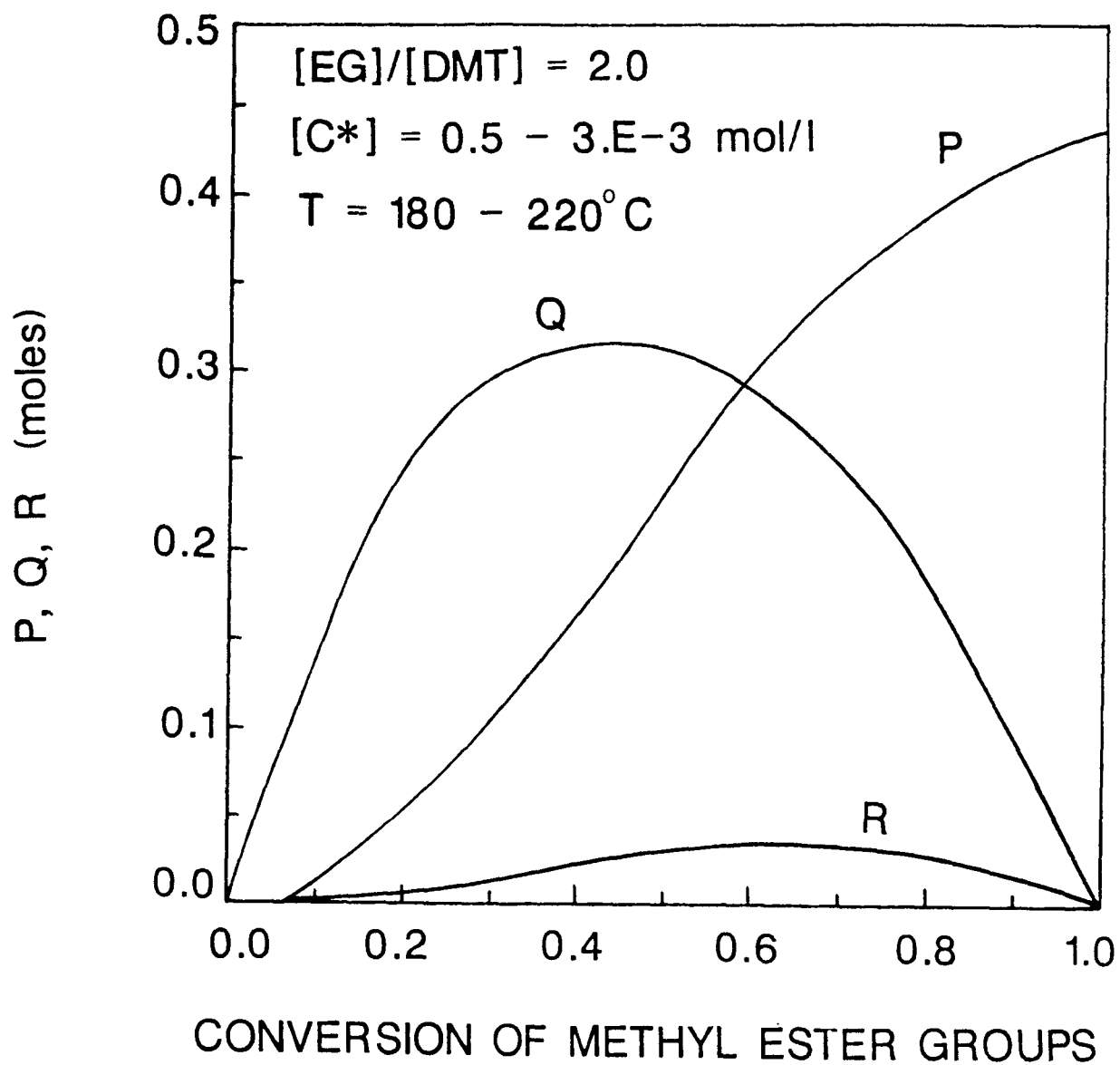


Figure 11 Total number of moles of oligomeric species for varying catalyst concentration and temperatures, [EG]/[DMT]=2.0.

indicated in Figure 11. Note that at high conversion (95%), there exist negligible amounts of Q_n and R_n -type oligomers. Thus, Figures 9-11 indicate that for a given $[EG]/[DMT]$ mole ratio, conversion of methyl ester end groups provides sufficiently detailed information on the product composition.

Effect of Reaction Temperature

When both $[EG]/[DMT]$ mole ratio and initial catalyst concentration are held constant the transesterification temperature can also influence the reaction rate and product composition distribution. Figure 12 shows the effect of reaction temperature on the conversion of methyl ester end groups. The degree of oligomerization and product composition distribution for various temperature are identical with those shown in Figures 9, 10 and 11. Figure 13 shows how mole numbers of various oligomeric species vary with reaction time at three different reaction temperatures. Both Figure 11 (concentration vs. conversion) and Figure 13 (concentration vs. reaction time) will give useful information required to operate the semi-batch transesterification reactor.

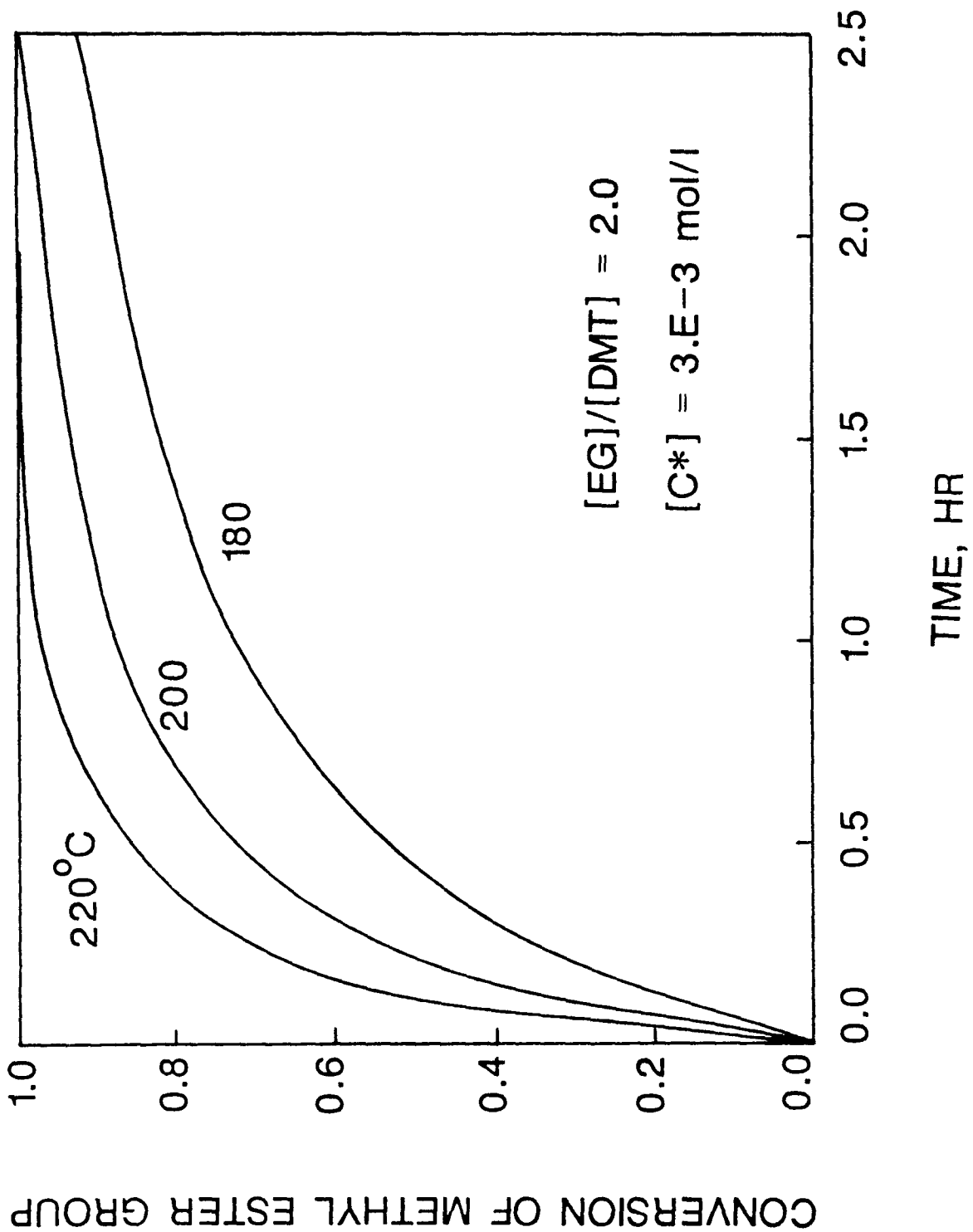


Figure 12 Effect of temperature on the conversion of methyl ester end groups.

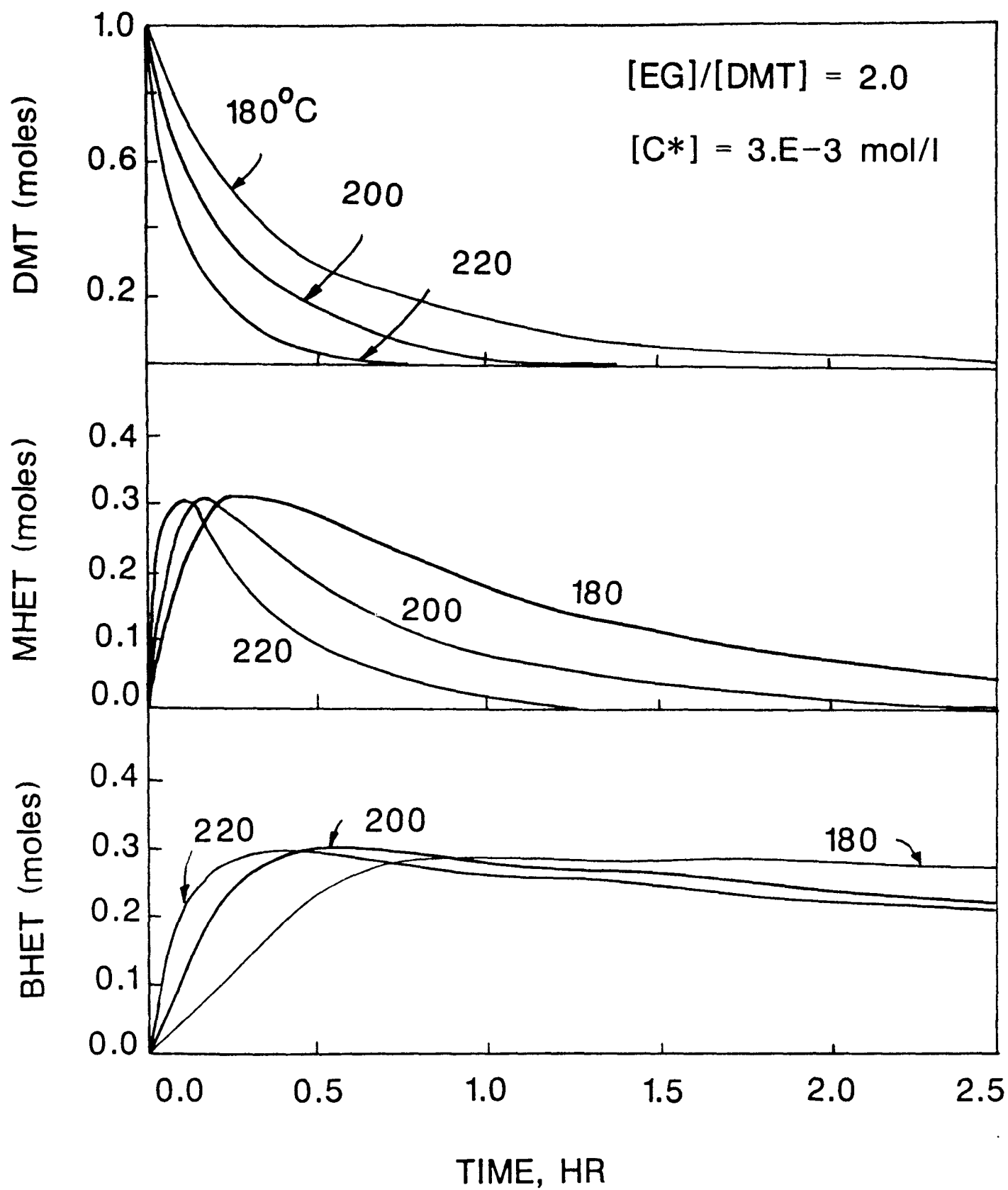


Figure 13 Product distribution for varying transesterification temperature.

IV. CONCLUDING REMARKS

A mathematical model of a semi-batch reactor for melt transesterification of dimethyl terephthalate with ethylene glycol has been developed and used to characterize the reaction kinetics and the composition distribution of the reaction product. In our modelling, all the reactive intermediates and raw materials containing functional end groups have been considered as independent molecular species. The model simulation indicates that both BHET and oligomers are the main constituents of the product. The oligomers produced at high conversion of methyl ester end groups for [EG]/[DMT] ratio of 2.0 - 2.5 are mostly dimers and have relatively narrow molecular weight distribution. Oligomers of longer chain length are produced when [EG]/[DMT] ratio is less than 2.0. It has been found that when the [EG]/[DMT] mole ratio is held constant, the effect of any factors affecting the reaction rate (i.e. catalyst concentration and temperature) can be represented by unique functions of the methyl ester group conversion. However, the conversion, the oligomer concentration and the oligomer molecular weights are strongly influenced by the variation in [EG]/[DMT] mole ratios.

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FIGURE CAPTIONS

- Figure 1 Effect of $[EG]/[DMT]$ mole ratio on the conversion of methyl ester group in a semi-batch reactor.
- Figure 2 Effect of $[EG]/[DMT]$ ratio on the product distribution.
- Figure 3 (a) Number average degree of oligomerization for varying $[EG]/[DMT]$ ratios.
(b) Weight average degree of oligomerization for varying $[EG]/[DMT]$ ratios.
- Figure 4 Average chain lengths of oligomers and oligomer concentration distribution for $[EG]/[DMT]=1.5$.
- Figure 5 Average chain lengths of oligomers and oligomer concentration distribution for $[EG]/[DMT]=2.5$.
- Figure 6 Conversion of methyl ester groups with and without oligomerization reactions.
- Figure 7 Formation of MHET and BHET in the absence of oligomerization reactions; $[C^*]=1.E-3$ mol/l, 200° C.
- Figure 8 Effect of catalyst concentration on the conversion of methyl ester end groups.
- Figure 9 Average oligomer chain lengths for varying catalyst concentrations and temperature, $[EG]/[DMT]=2.0$.
- Figure 10 Product composition distribution for varying catalyst concentration and temperatures, $[EG]/[DMT]=2.0$.
- Figure 11 Total number of moles of oligomeric species for varying catalyst concentration and temperatures, $[EG]/[DMT]=2.0$.
- Figure 12 Effect of temperature on the conversion of methyl ester end groups.
- Figure 13 Product distribution for varying transesterification temperature.